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# U.S. EPA Environmental Technology Verification Program Advanced Monitoring Systems (AMS) Center

# Water Stakeholder Committee Meeting Wednesday, February 21, 2007 Sacramento, CA

# **Meeting Minutes**

## **Agenda**

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Stakeholder Introductions Stakeholders

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Teresa Harten, US EPA

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Optical Property Measurements for Bryan Downing, USGS

High-Resolution Monitoring of Dynamic Systems

Technology Categories under Development Amy Dindal

(Chemical Oxygen Demand Technologies, Passive Ground Water Samplers, Nutrient Monitors, Estrogen Test Kits,

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Beach Monitoring, Lead Test Kits)

Next Water Technology Categories Amy Dindal/Stakeholders

Wrap up/Action Items Amy Dindal

## **Attendees**

#### **Stakeholder Committee Members:**

Martha Link, Nebraska Department of Environmental Quality (phone-in)

Lisa Olsen, USGS

Alan Mearns, National Oceanic and Atmospheric Administration

Vito Minei, Suffolk County Department of Health Services

Richard Sakaji, State of California Department of Health Services

Roy Spalding, University of Nebraska

Ken Wood, DuPont Corporate Environmental Engineering Group

#### **Observers:**

Jim Eychaner, USGS Stephanie Fong, California State Water Resources Control Board H. Kazemi, K&M Remediation, LLC. Peggy Lehman, California Department of Water Resources

## **EPA/Battelle ETV Program Staff:**

Bob Fuerst, EPA Teresa Harten, EPA Elizabeth Hunike, EPA Amy Dindal, Battelle Ryan James, Battelle

## **Guest Speakers:**

Bryan Downing, USGS Lorrie Flint, USGS

Trina Mackie, University of California, Berkeley and the Klamath Blue-Green Algae Workgroup

## **Welcome and Meeting Objectives**

Ms. Amy Dindal, Battelle AMS Center program manager, welcomed the stakeholders and observers to the meeting. She thanked Ms. Lisa Olsen for hosting the meeting at the United States Geological Survey (USGS). Ms. Dindal reviewed the agenda, and stated that the objectives for the meeting were similar to past meetings where the focus will be on verification testing progress and identifying priority technology categories for verification. Ms. Dindal also noted that there will be two speakers from USGS, Dr. Lorrie Flint and Mr. Bryan Downing, who will present on their respective programs.

## **Stakeholder Introductions**

For the benefit of the observers, each stakeholder introduced him or her self and described his or her role within his or her organization and interest in water monitoring.

#### **ETV Program Update and Sustainability Thoughts**

Ms. Teresa Harten, director of EPA's ETV program, provided an update on the ETV program. She began with a brief background on the ETV program and its successes, noting that it provides technology performance information that is critical to federal, state, and local agencies. Collaborations and vendor cost-sharing leverage ETV, generating approximately 40 to 50 percent of the total funds for the program. Ms. Harten further described that there have been 381 technology verifications and 85 generic protocols completed through the ETV program since 1995. Over 300 stakeholders are active in advisory groups and technical panels across the ETV program, and internet and worldwide interest in the program has resulted in greater than three million hits per year on the ETV web site, with interest continuing to grow.

Ms. Harten also stated that new case study booklets have been produced that document technology verifications and project future outcomes resulting from these verifications. She went on to describe a specific case study from one of the booklets, the verification testing of diesel retrofit technologies. Seven technologies were tested as part of this verification test, with six of them qualifying for EPA Office of Transportation and Air Quality (OTAQ) grant programs, such as the Clean School Bus Grant Program. As a result of the verification testing, at least 1,345 diesel retrofit technologies were sold. Ms. Harten pointed out that, over a seven-year period, because of these purchases, six to nine tons of particulate matter (PM) would be reduced and one life and \$3-5 million would be saved, based on risk reduction extrapolations using EPA's regulatory analysis for the Highway Diesel Rule. Over seven years at 10 percent projected market penetration, 9,000 to 31,000 tons of PM will be reduced, \$4-16 billion will be saved, and 683 to 2,380 people will avoid premature mortality.

Ms. Harten then proceeded to discuss graphical representations of statistics of the ETV program over the years. In a bar graph detailing ETV program verifications and funding sources, she showed how ETV base program funding has declined over the years, peaking in 1998 at just under \$10 million and declining to approximately \$2 million in 2006. The number of verifications has also decreased as base funding has declined, peaking at 57 verifications in 2000 and decreasing to 13 in 2006. Funding from other sources (not including in-kind contributions),

began contributing to ETV program funding in 1997 when the first verification tests were conducted and has continued in varying amounts over the next nine years. Ms. Harten then showed how the average time for completion of a verification test has increased over the years, taking from approximately 15 months in fiscal year 2002 to approximately 21 months in fiscal year 2006. She stated that increased collaborations have likely increased the time for verification.

The average cost per verification test or protocol development has varied over the past eight years (1998-2006), ranging from \$80,000 to \$300,000. Funding outside of ETV base program funding has also varied over time, though outside funding has increased over the past few years. Cost-sharing, cash, or in-kind support from outside groups is also a significant source of support for the ETV program. Ms. Harten showed how cost-sharing contributions to verification tests have varied between fiscal years 2002 and 2006. Direct funding, or cash, from other organizations has accounted for 25 to 85 percent of the total cost-share on verification tests and totaled \$840,000 in fiscal year 2006. In-kind support has consistently exceeded cash contributions, sometimes by as much as double (in fiscal year 2006). In-kind support has accounted for approximately 40 to 47 percent of the cost share in verification tests and ranged from \$1.3 million to \$2 million in estimated cash value.

Ms. Harten then turned her attention to the idea of sustainability. To better understand this area, she provided example sustainability metrics: recyclability, reusability, toxics use, resource (i.e., renewable or non-renewable), and life cycle analysis and impact analysis. She indicated that adding sustainability criteria to ETV verification tests would be ideal, but there are challenges. There would have to be agreement, through the use of the stakeholder process, on the appropriate sustainability criteria and how to measure and report these criteria. There would be additional costs associated with verification for these sustainability criteria. Also, the ETV program has been based on the fact that it provides third party testing data of a known quality. Ms. Harten indicated that sustainability criteria will rely largely on self-reporting by vendors, which means that the data for these criteria will be of an uncertain quality as they would not be a direct product of the ETV verification test. She pointed out that there would also be delays in reporting because of the likely challenges by vendors to presentation of the sustainability criteria results. It was pointed out that that AMS Center has often included sustainability criteria in its reports but has not called them "sustainability." It was agreed that the AMS Center should increase its focus on specifically calling out sustainability criteria.

#### **Current and Future Impact of the ETV Program**

Due to time constraints, this session was delayed for discussion in conjunction with the "Developing Technology Categories" discussion in the afternoon. Ms. Dindal asked the stakeholders to respond to the "homework" questions that were sent to the stakeholders before the meeting:

- What is one area in your field of expertise that has benefited from ETV tests? What direct results/benefits have you noted?
- In what other areas might ETV be able to make an impact? Where could an ETV test really be beneficial?

The stakeholders indicated that fact sheets and the ETV outcomes documents have been great outputs from the ETV program. In addition, the AMS Center's focus on rapid screening technologies has been impactful in many areas and something that the AMS Center should continue to focus on. The stakeholders also felt that the AMS Center should continue to foster collaborative relationships with groups such as National Oceanic and Atmospheric Administration (NOAA) and Department of Defense Environmental Security Technology Certification Program (DoD ESTCP). Other specific technology areas where ETV might make an impact were discussed in terms of future technology categories (see discussion on "Next Technology Categories").

## **AMS Center Update**

Ms. Dindal provided an AMS Center update. She reported that over its 10-year existence, 121 verification reports have been completed by the AMS Center. In addition, 22 test/QA plans have been completed, 37 stakeholder meetings have been held, and 84 AMS Center newsletters (*The Monitor*) have been published. She also said that seven technology verifications are currently in various stages of progress and numerous are under development. Ms. Dindal then listed the technology categories that the AMS Center has tested. Of the 121 verified technologies, 54 have been air monitoring technologies and 67 have been water monitoring technologies. Technologies verified by the AMS Center have ranged from ambient ammonia monitors to dioxin emissions monitors to atrazine ELISA test kits to on-line turbidimeters. Within each technology category, anywhere from one to 13 technologies have been verified by the AMS Center. There are six current, on-going AMS Center verification tests: mercury emission monitoring systems (4 technologies), personal cascade impactor sampler (1 technology), beach monitoring samplers (protocol development only), multi-parameter water sensors (1 technology), ballast water exchange screening tools (1 technology), and soil rapid toxicity technologies (protocol development only).

Ms. Dindal described recent outreach initiatives by the AMS Center: the November issue of *The Monitor* was distributed, AMS Center staff attended the February 7 Ohio Harmful Algal Bloom Focus Group Workshop as well as the February 11-14 National Air Quality Conference, and a manuscript to *Environmental Science and Technology* was in progress. Ms. Dindal also highlighted the support that the AMS Center has received over its existence. This includes \$685,000 in vendor contributions, \$581,000 in cash co-funding from collaborators, and \$3.68 million in in-kind support. Recent verification tests have been co-funded at or near 100 percent and vendor cost-share is increasing in certain market segments. Ms. Dindal noted that any new verification test must have funding support. She also indicated that stakeholders will be critical in the sustainability of the AMS Center. To this end, the stakeholders must continue to identify pressing environmental monitoring needs, identify and/or provide testing collaborations, and continue to take an interest in the AMS Center and its activities.

#### **Verification Status: Ballast Water Exchange**

Ms. Dindal gave an update on the status of the ballast water exchange verification test. To provide perspective on the test, Ms. Dindal provided some background information. She said that ballast water exchange at sea is one way to prevent aquatic invasive species from

contaminating a port. Mid-ocean ballast water exchange will become mandatory for vessels entering the US from outside the 200-mile exclusive economic zone. Thus, accurate, portable technologies for verifying this exchange are needed to support the regulation. Ms. Dindal said that the AMC Center had received stakeholder concurrence on pursuing a verification test in this technology category. Co-funding has been received from the US Coast Guard for this test, and vendor recruitment was completed. Only one vendor was identified with a viable technology for this test. Ms. Dindal identified the vendor as Dakota Technologies, Inc. Their technology is the BEAM 100 Ballast Water Assurance Meter. This device is a handheld unit that determines fluorescence from colored dissolved organic matter (CDOM) in ballast water. Stakeholders noted that they have heard of at least two other vendors that may have similar technologies coming to the commercial market: Turner Design and Wet Labs. Ms. Dindal indicated that the AMS Center will contact these vendors to see if there would be interest in participating in a second round of testing of ballast water exchange screening tools.

Ms. Dindal said that a test/QA plan had been prepared and finalized for this verification test and peer reviewers have been obtained. The test will compare the BEAM 100 to lab bench-scale fluorescence measurements. This will be a laboratory-based test only; there will be no field testing conducted. Ms. Dindal then outlined the test parameters to be assessed on the BEAM 100, which includes: accuracy, linearity, precision, method detection limit, inter-unit reproducibility, temperature effects, matrix effects, data completeness, and operational factors. Accuracy, linearity, precision, and temperature effects will be assessed by using varying levels of quinine sulfates and fulvic acid prepared in HPLC-grade water. The stakeholders asked why B&J organic-free HPLC-grade water was selected. Feedback from the Verification Test Coordinator, Mary Schrock, after the meeting was that this was the type of water recommended by the reference laboratory instrument operator as good background water for ultraviolet (UV) measurements. The HPLC-grade water was also test-checked for interference in the UV wavelengths of interest and it was fine, so this was the water that was selected. Seven measurements of this solution will be taken to determine method detection limits. Ms. Dindal indicated that two BEAM 100 units will be tested side by side to determine inter-unit reproducibility while matrix effects will be determined using 10 open ocean and coastal water samples. Operational factors will include ease of use, maintenance and calibration needs, consumables, waste generation, and sample throughput. Ms. Dindal then detailed the locations from which the "real world" open water samples will be obtained. These include waters in Massachusetts, Florida, Washington, New York, California, and Rhode Island. Testing for the ballast water exchange verification test is scheduled to take place in February-March 2007, with the data analysis for the verification report to be prepared in March-April 2007.

## Sensicore Test/QA Plan Discussion

Dr. Ryan James of Battelle presented the test/QA plan for the Sensicore multi-parameter sensor verification test. He said that the Sensicore technology could measure 10 different parameters, including free chlorine, pH, conductivity, and temperature. The sensor is a grab sampling device that can provide results in four minutes. Dr. James then outlined the verification testing progress. He said that the vendor has made a significant contribution to the cost-share for this test. EPA's National Exposure Research Laboratory (NERL) Ecological Exposure Research Division contributed pre-test field measurements in September and the City of Columbus, Ohio

is contributing lab and field testing. Testing is expected to begin in April 2007, as there was a delay in the start of the test due to the vendor completing a software update on the instrument.

Dr. James indicated that the EPA pre-field test took place at Shaylor's Run off the East Fork of the Little Miami River. For this stage of the test, the Sensicore technology was put through a qualitative evaluation in a field setting. Stage 2 of the experimental plan for the Sensicore verification test will involve laboratory testing of deionized water samples. Dr. James said that this testing will involve various concentration levels of different test solutions to determine the technology's ability to estimate different water quality parameters, including pH, calcium, ammonia, and oxidation/reduction potential. Stage 3 of the verification test will involve lab and field testing of drinking and surface water samples. All of the samples will be from the Columbus, Ohio water system, which is a chlorinated system. A total of 10 samples will be tested, two as field samples. All of the samples will be analyzed in triplicate, with a comparison to a reference analyses, and two identical Sensicore units will be tested simultaneously. Dr. James reiterated that the Stage 1 pre-field testing has already been completed. The test/QA plan has been written and Stage 2 and 3 testing is set to occur in March-April 2007.

# <u>Klamath Region Blue-Green Algae Working Group and Overview of the Microcystin</u> Problem

Ms. Trina Mackie of the University of California, Berkeley gave a presentation on blue-green algae based on experiences with the Klamath River Basin, located in Southern Oregon and Northern California. Ms. Mackie is part of the Klamath Blue-Green Algae (BGA) Working Group. She said that this group convened officially in spring 2006 with its main task to oversee and administer funding provided by PacifiCorp under a settlement agreement for a research study to identify issues associated with blue-green algae and its toxins in the Klamath River Basin. The working group includes representatives from various agencies and groups, including EPA, local county health agencies, Oregon Department of Fish and Wildlife, and the US Bureau of Reclamation. Ms. Mackie noted that the main concerns with blue-green algae are that it is a public health risk, it is an ecological risk, and there are aesthetic and odor issues associated with its presence. She also pointed out more than a dozen water bodies throughout northern California that are impacted by blue-green algae.

The Klamath River Basin is an area of particular concern. Ms. Mackie said that waters in the Klamath Basin exceed state water quality standards on both sides of the border. Specific problems include high nutrient levels, high temperatures, low dissolved oxygen, and high pH levels. These are prime conditions for cyanobacterial or blue-green algae blooms. For a broader perspective, Ms. Mackie gave a brief history of blue-green algae in the Klamath River Watershed. In 1978, an eutrophication study was conducted, where it was determined that the nitrogen input from Iron Gate Reservoir far exceeded the nitrogen output. Mycrosystis and microcystins were documented in 2004-2006 in the Iron Gate and Copco Reservoirs. An advisory was put out in 1996 at Agency Lake because of periodic microcystis blooms. Ms. Mackie also said that the Upper Klamath Lake had very low microcystis cell counts from 1990-1997 but showed regular aphanizomenon blooms.

As part of the Klamath River Watershed project, there are 17 sampling sites throughout the basin. Ms. Mackie said that the general sampling strategy is to collect grab samples from shoreline and open-water sites and split them with a churn splitter. Sampling for cell density and toxin quantification is conducted bi-monthly, but toxin analyses are not conducted until toxic blue-green algae species are detected. Ms. Mackie noted that not all of the sites in the basin are sampled equally and that data on other water quality parameters are also collected with varying frequency by site and parameter. She also said that field work was initiated by the Yurok and Karuk Tribes.

She then showed some monitoring data from 2005 and 2006 for the Iron Gate and Copco Reservoirs and the downstream monitoring sites on the main stem of the Klamath River. She described trends in both the *Microcystis aeruginosa* (MSAE) cell density and the microcystin concentrations. The sites in the reservoirs had an MSAE cell density that exceeded the World Health Organization (WHO) Moderate Probability of Adverse Health Effects Level (MPAHEL), while sites downstream of the reservoirs in the main stem of the river only occasionally reached levels of public health concern. For most stations, there were also large fluctuations in MSAE cell density throughout the bloom season when the water is monitored (May to November). Cell counts peak in mid- to late summer and then the population declines and senesces, usually completely subsiding by the end of October. The microcystin concentrations follow the same spatial and temporal trends as the cell counts, but there is usually about a two-week lapse between the peak in cell counts and the peak in microcystin concentrations.

Ms. Mackie showed the temporal variation in microcystis cell counts for one site in the Klamath River Basin. Counts were highest in late July 2006 and then declined by almost three orders of magnitude over the summer. Ms. Mackie noted that there were also spatial variations in microcystis cell counts in the basin. Cyanotoxin cell concentrations varied considerably over time, even over the span of approximately one month. Levels jumped from approximately 3,000  $\mu$ g/L to 12,000  $\mu$ g/L for one particular reservoir site from July 27, 2006 to August 8, 2006. There was also strong spatial variation in the Klamath microcystin concentrations.

Ms. Mackie pointed out that there are some data issues with this project. Sample collection, toxin quantification, and data reporting all have potential issues that must be dealt with. Laboratories have been using an extremely low reporting limit that the work group has not been able to substantiate. They are therefore not confident in any data reported below 1 (parts per billion) ppb total microcystin. The work group has decided to list results as below the reporting limit if they are less than 1 ppb. The reservoir data is so much higher than 1 ppb that this is not an issue, but in the main stem concentrations can be quite low. Other issues that Ms. Mackie discussed include the data discrepancies in the liquid chromatography/mass spectrometry (LC/MS) results from two different laboratories, with microcystin concentrations being in some cases orders of magnitude apart between the two measurements.

Ms. Mackie then showed how different the results were for calibration standard from different suppliers. The standard purities differed widely. Ms. Mackie described the possible sources of error in the data obtained from the Klamath River Basin. She said that sample splitting, adhesion of toxins to sample containers, sample preparation, equipment operation, and calibration standards are all sources of potential error. Ms. Mackie then outlined the research needs that still

remain. These include the verification of the purity of standards and the standardization of sample preparation and cell lysis protocols. Other needs include inter-laboratory validation comparison and certification and better systematic comparison of analytical methods.

#### **Verification Status: Microcystin Technologies**

Dr. James discussed the chronology of events regarding a potential verification test for immunoassay test kits for algal toxins. He said that in August 2005, stakeholders recommended that the AMS Center pursue this technology category; the AMS Center applied, unsuccessfully, to the Nebraska Environmental Fund for co-funding to support a verification test. By May 2006, the AMS Center became aware of the severe blue-algae problems in the Klamath Region and sought interested organizations for partnering in a verification test. In the same month, Dr. James presented the idea of an ETV verification test at a California Statewide Blue-Green Algae Workshop. The California Water Resources Board developed as a possible co-funding opportunity, and the Karuk Tribe, US EPA, and others were anxious to provide in-kind support. In September 2006, Dr. James spoke with EPA NERL, who had an interest in the verification test and suggested the state of Florida and EPA NCER as possible partners. In January 2007, Dr. James continued his participation in the Klamath Blue-Green Algae Workgroup and heard conclusively that the California Water Resources Board, while interested, would not be able to co-fund a verification test. In February 2007, Dr. James attended the Ohio Harmful Algal Bloom Workshop at NOAA in Toledo, Ohio and identified several possible in-kind supporters. A discussion ensued amongst the stakeholders on whether or not the AMS Center should continue to actively pursue this verification test. There was a discussion regarding the point raised during Ms. Mackie's presentation, which was whether or not the time was right for pursuing testing of immunoassay kits when there currently are issues with calibration standards for microcystins. It was pointed out that these kits are being used on a daily basis without independent confirmation of performance, so it would be best to pursue sooner as opposed to later. There was also discussion regarding the content of the testing, and the stakeholders agreed that, if a test was pursued in the near-term, due to the potential issues with calibration standards, that the test should focus on screening applications of the immunoassay kits and not necessarily comparability to the LC/MS method.

# <u>Application of Stream Temperature Measurements to Ecological Health in the Klamath River Basin</u>

Dr. Lorrie Flint of the USGS presented information related to the application of stream temperature measurements to ecological health in the Klamath River Basin. Dr. Flint started by presenting an overview of her talk, noting that she would discuss the rationale for temperature measurements in the Klamath Basin, the scales of such investigations, examples of the methods that are used, and a possible sensor testing approach.

Dr. Flint said that the Chinook salmon population was declining in the Klamath River. Their numbers are expected to fall below a minimum spawning target for the third straight year, triggering a ban in fishing. Dr. Flint noted, however, that Chinook salmon populations in the Central Valley are abundant and were last measured in 2006 at more that 10 times the number of spawning fish found in the Klamath River. Dr. Flint indicated that the proposed ban on salmon

fishing in the Klamath River Basin in 2006 was predicted to adversely impact the fishing industry in that area, possibly leading to bankruptcy for some. She indicated that 70,000 fish, including 35,000 Chinook salmon, were killed by disease and suffocation when they fell into stagnant pools of water on the lower Klamath. In 2003, the US Fish and Wildlife Service reported that this was the worst die-off in the history of the Klamath and blamed the deaths on a combination of low water flows and a relatively large spawning run.

Dr. Flint said that the US Bureau of Reclamation (USBR) still follows the same water diversion policy that it did in 2002, but the USBR says that they control water that represents only 11 percent of the flow at the mouth of the Klamath, indicating that this practice makes it hard for them to make significant impacts on the ecosystem in the river. The National Academy of Sciences panel supported the USBR view by determining the culprits in the fish die-off to be high water temperatures; sedimentation caused by logging, road construction, and agriculture; and localized poor water quality.

Dr. Flint said that the needs for stream temperature measurements in the lower Klamath Basin occur at various scales. For example, water quality models that require tributary boundary conditions, such as water temperature, are being developed in support of the Federal Energy Regulatory Commission (FERC) relicensing process and in support of the development of Total Maximum Daily Loads (TMDLs). In another instance, stream temperatures are needed for habitat assessments to understand processes such as nutrient cycling, fish diseases, and spawning, rearing, and holding habits. Dr. Flint then showed plots of point measurements of stream temperatures taken at the mouths of the tributaries to the mainstem of the Klamath River between 2002 and 2003. In 2002, temperatures at the mainstem were above or within the range for chronic or acute salmon stress from July through September. Temperatures exhibited a similar pattern in 2003. Dr. Flint said that water temperatures are variably sensitive to different meteorological and stream parameters. Air temperature and the percent of shade encompassing the stream have the greatest impact on overall water temperature.

Dr. Flint said that one approach is to develop the relationship between energy balance parameters, air temperature, and stream temperature on measured tributaries. Another approach would be to use simple regression models to extrapolate stream temperature to unmeasured tributaries and fill in the gaps for measured tributaries. She then presented an application of spatially distributing energy balance parameters, air temperature, and relative humidity. She used data from the National Climatic Data Center, the Remote Automated Weather Stations, the Solar and Meteorological Surface Observation Network, and the California Irrigation Management Information System plotted over the Klamath River Basin study area. Dr. Flint showed maps of spatially distributed maximum air temperature, topographic shading cloudiness, and incoming solar radiation (modeled using topographic shading and cloudiness) for a given day (May 15, 2003). Dr. Flint also showed a map of solar radiation for the rivers and tributaries in the lower Klamath River Basin, in which color scales of radiation were only shown for the paths of the river.

Dr. Flint then showed multiple regressions of maximum and minimum air temperature, radiation, vapor density deficit, and day angle function. The results of the regressions were then plotted for maximum and minimum daily air temperatures, individually, as the predicted stream

temperatures versus the measured stream temperatures. For both maximum and minimum air temperature, the fit of the modeled and measured data was linear with a slope of one and a R<sup>2</sup> of 97 percent in both cases. Using the modeled data, Dr. Flint demonstrated how stream temperature could be extrapolated to unmeasured days for four years and also to nearby unmeasured basins.

Dr. Flint then moved on to discuss stream temperature and methods of measurement. She asked if a point measurement truly represents the temperature of the general habitat in a tributary or that of the main stem. She also pondered whether such a measurement represents what the fish actually experience. Dr. Flint said that methods for measuring stream temperature include point measurements and distributed fiber-optic temperature sensing. Point measurements can be for one point in time where thermocouples, thermometers, or similar instruments are used and satellite infrared measurements are in 2-D representations. Or, point measurements can be continuous measurements where data sondes, such as multi-parameter water probes, are used and datalogging sensors are employed. Distributed fiber-optic sensors take 1-D measurements every meter for thousands of meters. Dr. Flint pointed out that, in making these measurements, the question becomes where in the cross section of the stream to put the sensor and how best to represent what the fish experience. One option is to install a passive integrated transponder (PIT) into the fish to detect their location. A temperature sensor can be incorporated into the PIT to better track water temperatures that the fish experience.

Dr. Flint said that there are things to take into consideration when determining the sensor to use for temperature measurements. The application needs to be considered, such as the scale or habitat, any seasonality issues, the needed accuracy, and the installation requirements. Also, the cost of the sensor and the personnel needed to operate it along with the availability of the sampler need to be taken into consideration. She then provided some examples of potential temperature sensors. The TidbiT Data Logger is a temperature data logger with 12-bit resolution and a wide temperature range. It has been used on dogs and luggage and is waterproof up to 300 meters. Hydrolab produces a continuous recording data sonde that contains multiple sensors, including temperature. Dr. Flint said that fiber optics are also a good sensor choice. They are relatively inexpensive; therefore, kilometers of them can be installed. They span the critical scale from 0.05 meters to 5,000 meters and provide continuous measurements in time and space. The precision of the fiber optics allows mass balances to be calculated with greater precision and less uncertainty. Fiber optics are being used in Maibich, Luxembourg to monitor the temperature of a stream. The goals of this project are to quantify the locations of surface water/groundwater interactions. The fiber optics provide continuous spatial/temporal data along an entire first order stream. To verify the performance of these various temperature sensors, Dr. Flint suggested that a sonde be tested at a downstream point, that datalogging sensors such as the TidbiT, SugarCube, I-Button, or TinyTag be placed side-by-side at several cross sections, that fiber optic cables be placed at three to four positions across the channel extending three to five kilometers, and that fish with PIT temperature tags also be tested.

In summary, Dr. Flint said that stream temperature measurements are imperative to understanding the ecological system in the Klamath Basin. Various methods can be applied to investigate stream processes at different scales but the sensor choice for monitoring temperature is dependent on the proposed application. She indicated that the comparison of temperature

sensing methods will provide a better understanding of the system and what the measured temperature represents.

#### Optical Property Measurements for High-Resolution Monitoring of Dynamic Systems

Mr. Bryan Downing of USGS gave a presentation on optical property measurements for high-resolution monitoring of dissolved organic matter (DOM) in dynamic systems. He first presented a brief overview of the optical properties of absorption and fluorescence. He indicated that these kinds of measurements were relatively inexpensive and easy to perform and may be used to understand DOM processes across space and time as well as to understand the non-carbon specific processes, such as nitrate cycling.

Mr. Downing discussed the application of optical property measurements using discrete samples. He explained how a D-77 depth integrated sampler was used to acquire samples for optical analyses, dissolved organic carbon (DOC) analysis and disinfection byproducts (DBP), such as trihalomethanes (THM). Further, optional properties and analyses of DOC and THM were used to model the system under study or calibrate in-situ instrumentation. He then described how the modeling aspect of such samples might work; saying that the optical properties would be first broken down by spectral decomposition and then, through the use of multivariate regression and analysis, predicted values of a measured variable (i.e., DOC, THM) could be determined from the actual (observed) sample values. Mr. Downing showed an example of this modeling aspect by showing graphs of predicted versus observed values for disinfection byproduct information.

Mr. Downing then moved on to discuss the use of in-situ instrumentation to collect high frequency time series of these same measured variables in various studies. He described a flow through instrumentation system comprised of fluorometers, photometers, and ancillary sensors, designed to measure optical properties in-situ. Optical measurements were made using WetLabs model colored dissolved organic matter (CDOM), and chlorophyll-A (Chl-A) fluorometers. A WetLabs model AC9 spectrophotometer and Satlantic model ISUS IV- spectrophotometer were used to measure absorption and backscatter. Ancillary chemical and physical information were collected using a Hydrolab DS-4 model CTD, Aanderaa optical dissolved oxygen sensor and a SonTek model acoustic doppler current profiler (ADCP) to measure water velocity. He explained that measuring chemical and physical properties in-situ at high sampling frequencies are necessary to explore DOM (e.g., DOC, THM) and nutrient (e.g., NO3) cycling.

#### **Technology Categories under Development**

Ms. Dindal discussed technology categories under development at the AMS Center. She first spoke about chemical oxygen demand (COD) analyzers. Aqua Diagnostics of Australia has agreed to fund a verification test of their PeCOD analyzer. This technology uses photoelectrochemistry to determine COD levels. A known small volume of sample is mixed with an electrolyte solution and introduced into an analysis cell. Then, a titanium dioxide sensor is illuminated to create a powerful oxidizing agent that oxidizes all organic material present. Ms. Dindal said that the vendor claims that the PeCOD analyzer has a detection limit of 0.1 parts per million (ppm), a reproducibility with <2 percent relative standard deviation, and a detection time of <180 seconds on average.

Ms. Dindal said that the AMS Center staff will collaborate with DuPont to conduct this verification test, and recognized Mr. Ken Wood for his leadership. The test will be performed at DuPont's wastewater lab in Wilmington, Delaware where a variety of wastewater samples will be used to challenge the analyzer. Ms. Dindal said that there is the potential for on-line testing to take place in a test reactor or possibly a nearby DuPont plant. The AMS Center expects a signed vendor agreement in early March with testing to begin in spring 2007. Ms. Dindal then asked for volunteers from the stakeholder committee to serve as peer reviewers.

Ms. Dindal next described COD test kits developed by Hach. There are two kits of interest, the dichromate method (Reactor Method 8000) and the manganese III COD method. The dichromate method is EPA approved and requires that a sample be heated for two hours and cooled to room temperature before analysis. The manganese III COD method is not approved for compliance testing but allows the user to complete up to 25 tests in less than 90 minutes. Unlike the dichromate method, which produces metal wastes, there is no such waste with the manganese III COD method. This is important because a technology like the PeCOD analyzer from Aqua Diagnostics would demonstrate significant sustainability criteria being met with this verification, due to the elimination of heavy metal reagents (both from use and disposal aspects) and long sample preparation times.

Passive ground water samplers are another potential technology category. Ms. Dindal said that concurrence was received from the stakeholders on this category. At this point, only one vendor, Dakota Technologies Inc., is interested in verification testing. They market a closed-loop, noflow sampling technique. She noted that this vendor was seeking approval of Small Business Innovative Research (SBIR) grant funds to fund approximately 100 percent of the verification test. She also indicated that the AMS Center will possibly pursue joint verification with the DoD's ESTCP.

Ms. Dindal then moved on to discuss nutrient analyzers. She indicated that this technology has industrial and environmental applications. ETV verification for industrial applications occurred in 2005 in collaboration with DuPont. Ms. Dindal said there has been vendor interest from Greenspan, EnviroTech, and others in an environmental application verification test; however, at this point, the AMS Center is in need of co-funding to proceed with this verification test.

Estrogen ELISA kits are another technology category under development. Ms. Dindal explained that EPA Regional Science Liaison Ron Landy (Region 3) had interest and limited funding to support a verification test for this technology category. Three commercial vendors were identified for this category: Abraxis, Wako, and Biosense Laboratories. Ms. Dindal said that an EPA interagency work group decided to pursue a small-scale, round robin evaluation of the Abraxis test kit. The hope is that this small-scale study will invoke support for broader ETV tests in this area.

The beach monitoring technologies verification test was cancelled recently because of the withdrawal of several vendors. Ms. Dindal said that the AMS Center is working on a generic protocol for rapid screening technologies for beach water quality, including both qualitative and

quantitative technologies. Peer review of the protocol is expected soon, with a completed protocol to be done before summer 2007.

One vendor from the beach monitoring test that did not withdrawal was B2P Limited of New Zealand. They make the Coliquik<sup>TM</sup> test kit for coliform and  $E.\ coli$ . Ms. Dindal said that this vendor has had interest from groups hit by  $E.\ coli$  issues and is interested in testing in the summer 2007. The expectation is that B2P will help to identify collaborators and fund a significant portion of the test.

Finally, a verification test for drinking water test kits for lead is under consideration. Ms. Dindal said that Silver Lake Research has approached the AMS Center about verifying their Watersafe® drinking water test kit. The company sells a commercially available test kit targeted towards consumers. The technology is qualitative and is a 10-minute immunoassay test similar to a home pregnancy test. Ms. Dindal asked if there was stakeholder concurrence on proceeding with this technology verification and, if so, if there were any volunteers to serve as peer reviewers. This was discussed during the next water technology categories discussion.

# **Next Water Technology Categories**

Ms. Dindal discussed water technology categories to pursue with the stakeholder group. She said that the purpose of this discussion was to determine verification priorities for the discussed technology categories, provide new technology category recommendations, and also discuss the information needed to proceed with a new technology category. Specifically, before proceeding with a new category, the AMS Center needs the names of vendors with commercial technologies, the names of potential collaborators, and the names of stakeholders interested in supporting a verification test for that category. In considering what technology categories to prioritize, Ms. Dindal said that stakeholders should consider the feasibility of verifying such a technology, the number of commercially available technologies, and what outcomes might result from a verification test. Ms. Dindal then reminded the group of the collaboration needs for a verification test, which include co-funding, test site host, on-site staff, reference method sampling and analyses, and possibly the hosting and preparation of a technology field day.

To put current technology category recommendations into perspective, Ms. Dindal reviewed previous stakeholder meeting minutes to discuss what technology categories have been suggested in the past. She first focused on the water stakeholder meeting in Seattle, Washington in 1998. The water monitoring technology categories suggested at that meeting ranged from home test kits for pathogens in drinking water to chemical-specific field probes for volatile organic compounds (VOCs) in groundwater to turbidimeters to on-line monitoring technologies for disinfectants. Ms. Dindal noted that over the years, 13percent of the technology category suggestions by stakeholders have been for monitoring organic compounds, 19 percent have been for monitoring physical parameters, 30 percent have been for monitoring inorganic compounds, and 38 percent have been for monitoring biological species. However, in terms of actual verification tests, she pointed out that the split was 20 percent for organic compounds, 23 percent for biological species, 27 percent for inorganic compounds, and 30 percent for physical parameters. Ms. Dindal then listed some recent technology category suggestions, which

included in-situ algal monitors, perchlorate monitors, and hyperspectral remote sensing technologies, as well as technologies discussed as "under development" previously.

Ms. Dindal asked the stakeholders to consider various criteria for each new technology category suggested. They should consider if the technology category is well-defined, whether it is still important to verify, if there are commercially available technologies on the market, who potential test collaborators could be, and which stakeholders have an interest in or experience with this technology.

This list of technology categories suggested by the stakeholders included the following. Those categories in **bold** received the stakeholders concurrence.

# Microcystin ELISA kits/in-situ algal monitors

Perchlorate monitors
Dissolved oxygen monitors
Temperature sensors
Nutrient monitors for environmental applications
Lead drinking water test kits
Estrogen ELISA kits

*E.coli* test kits Flowmeters

**Multi-parameter monitors (including turbidity sensors)** 

Hyperspectral remote sensors

**UV** sensors

# Wrap up/Action Items

Ms. Dindal closed the meeting by saying that the AMS Center would continue to conduct teleconferences with the stakeholders on a quarterly basis. The next water stakeholder call will be in late spring/early summer. Ms. Dindal thanked the stakeholders for their active participation in the meeting.